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PATENT

TITLE SHEET

Title: ETHYLENE POLYMERIZATION EMPLOYING BIS-IMINO PYRIDINYL
TRANSITION METAL CATALYST COMPONENTS

**ETHYLENE POLYMERIZATION EMPLOYING BIS-IMINO PYRIDINYL
TRANSITION METAL CATALYST COMPONENTS**

FIELD OF THE INVENTION

[0001] This invention relates to the polymerization of ethylene employing bis-imino pyridinyl transition metal catalyst components of C₂, C_{2v} and C_s symmetry to produce ethylene polymers and more particularly, to the use of such catalyst components to control polymer yield and molecular weight.

BACKGROUND OF THE INVENTION

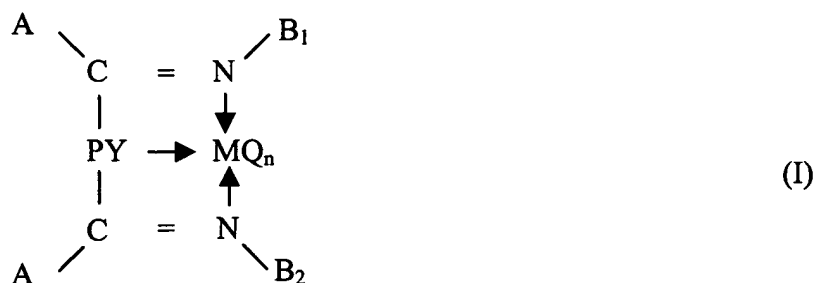
[0002] Ethylene polymers such as polyethylene homopolymers and ethylene-propylene copolymers may be produced under various polymerization conditions and employing various polymerization catalysts. Such polymerization catalysts include Ziegler-Natta catalysts and non-Ziegler-Natta catalysts, such as metallocenes and other transition metal catalysts which are typically employed in conjunction with one or more co-catalysts. The polymerization catalysts may be supported or unsupported.

[0003] Ethylene homopolymers or copolymers may be produced under various conditions in polymerization reactors which may be batch type reactors or continuous reactors. Continuous polymerization reactors typically take the form of loop-type reactors in which the monomer stream is continuously introduced and a polymer product is continuously withdrawn. For example, the production of polymers such as polyethylene or ethylene-propylene copolymers involve the introduction of the monomer stream into the continuous loop-type reactor along with an appropriate catalyst system to produce the desired ethylene homopolymer or copolymer. The resulting polymer is withdrawn from the loop-type reactor in the form of a "fluff" which is then processed to produce the polymer as a raw material in particulate form as pellets or granules. It is often the practice in the production of ethylene homopolymers and ethylene C₃₊ alpha olefin copolymers to employ substantial amounts of molecular weight regulators such as hydrogen to arrive at polymers or copolymers of the desired molecular weight. Typically in the polymerization of ethylene, hydrogen may be employed as a regulator with the hydrogen being introduced into the monomer feed stream in amounts of about 10 mole % and higher of the ethylene feed stream.

SUMMARY OF THE INVENTION

[0004] In accordance with the present invention, there are provided ethylene polymerization processes employing bis-imino pyridinyl transition metal components which exhibit C₂, C_{2v} and C_s symmetry. The transition metal catalyst components of different symmetries may be employed to control polymerization characteristics and characteristics of the resulting polymer products. Alternatively, transition metal catalyst components of the same symmetry may be employed with variations in the bulk or characteristics of the ligand components being used to control factors such as polymer yield and polymer molecular weight.

[0005] In carrying out the present invention, there is provided a transition metal catalyst component having C₂, C_{2v} or C_s symmetry and characterized by the formula:



[0006] In formula (I), M is a Group 4-11 transition metal, n is an integer within the range of 1-3, Q is a halogen or a C₁ – C₂ alkyl group, and PY is a pyridinyl group which is coordinated with M through the nitrogen atom of the pyridinyl group. Further, with respect to formula (I), A is a methyl group, a phenyl group, or a substituted phenyl group and said catalyst component has C₂ symmetry and B₁ and B₂ are the same and are a 1-naphthyl group, a substituted 1-naphthyl group, a 5,6,7,8-tetrahydro-1-naphthyl group or an anthracenyl group, or said catalyst component exhibits C_{2v} symmetry and B₁ and B₂ are the same and are a phenyl group or a substituted phenyl group, or said catalyst component exhibits C_s symmetry and B₁ is

a phenyl or substituted phenyl group and B₂ is different from B₁ and is a polyphenyl group or terphenyl group. There is also provided an activating co-catalyst component. The catalyst component and said co-catalyst component are contacted with ethylene in a polymerization reaction zone which is free of hydrogen or contains hydrogen in an amount which is less than 5 mole % of the ethylene under polymerization conditions to produce a polymer product by the polymerization of the ethylene followed by recovering said polymer product from the reaction zone. As indicated above, the ethylene polymerization procedure may be carried out using small amounts of hydrogen as a regulator. However, the use of hydrogen or another molecular weight regulator is not necessary and molecular weights can be controlled by controlling the symmetry of the transition metal catalyst component employed in the invention. As noted previously, the polymer product can be a ethylene homopolymer or a copolymer of ethylene and C₃₊ alpha olefin, specifically an ethylene-propylene copolymer.

[0007] In one embodiment of the invention, the catalyst component introduced into the polymerization reaction zone comprises a mixture of two catalyst subcomponents, one of which exhibits C₂, C_{2v} or C_s symmetry and the other of which exhibits C₂, C_{2v} or C_s symmetry which is different from the symmetry of the first subcomponent. In a further embodiment of the invention, a catalyst component is employed which exhibits C₂ symmetry to produce a polymer of lower molecular weight than the polymer produced by a corresponding catalyst component of C₂ symmetry in which the substituents A are of a higher molecular weight than the substituents A of the catalyst component, or in which the groups B₁ and B₂ are less aromatic than the groups B₁ and B₂ of the catalyst component. Where a catalyst component exhibiting C_s symmetry is employed, the process produces a polymer of higher molecular weight than the polymer

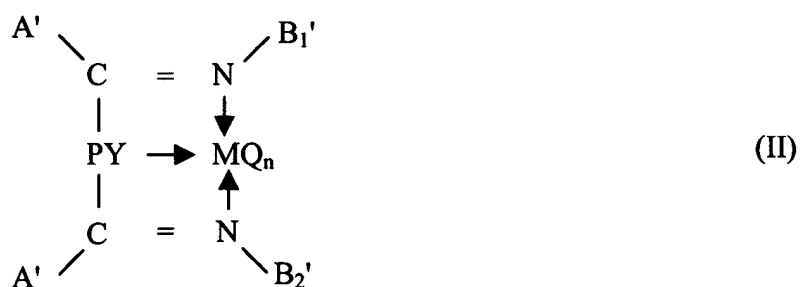
produced by a corresponding catalyst component of Cs symmetry in which at least one of the groups B₁ and B₂ is less bulky than the corresponding group B₁ and B₂ of the catalyst component. In a further embodiment of the invention employing a catalyst component which exhibits C_{2v} symmetry, a polymer product of higher molecular weight is produced than the polymer produced by a corresponding catalyst component of C_{2v} symmetry in which substituents A are of a lower molecular weight than the substituents A of the catalyst component.

[0008] In another aspect of the invention, the catalyst component exhibits C₂ symmetry to produce a polymer product having a lower molecular weight than the polymer product produced by polymerization under the same conditions with a catalyst component having Cs or C₂ symmetry. Where the catalyst component exhibits C_{2v} symmetry, the polymerization product is operated under conditions to produce a polymer product having a molecular weight greater than that produced by the reaction zone under corresponding conditions with the catalyst having Cs symmetry.

[0009] In a preferred embodiment of the invention, M in formula (I) is a transition metal selected from the Group 8-10 of the Periodic Table of Elements. Preferably, M is iron or cobalt, n is 2 and Q is chlorine or bromine.

[0010] As noted previously, hydrogen need not be employed in the polymerization procedure. Where hydrogen is employed, it preferably is introduced in an amount to provide a hydrogen-ethylene mole ratio within the range of 0.001 – 0.02. The hydrogen can be employed to increase the activity of the catalyst component relative to the activity of the catalyst component without the introduction of hydrogen.

[0011] In another embodiment of the invention, there is provided an ethylene polymerization process using first and second transition metal catalyst components. The first transition metal catalyst component is characterized by the formula (I) as described above. This transition metal catalyst component, along with a first activating co-catalyst component, is contacted with ethylene in a polymerization reaction zone under polymerization conditions to produce a first polymer product by the polymerization of the ethylene. This polymer product is recovered from the reaction zone. There is further provided a second transition metal catalyst component of C₂, C_{2v} or C_s symmetry which is different than said first transition metal catalyst component and is characterized by the formula:



wherein M is a transition metal selected from Groups 4-11 of the Periodic Table of Elements, n is an integer of from 1 – 3, Q is a halogen or a C₁ – C₂ alkyl group, PY is a pyridinyl group, which is coordinated with M through the nitrogen atom of said pyridinyl group, A' is a methyl group, a phenyl group, or a substituted phenyl group and said second catalyst component has C₂ symmetry and B₁' and B₂' are the same and are a 1-naphthyl group, a substituted 1-naphthyl group, a 5,6,7,8-tetrahydro-1-naphthyl group or an anthracenyl group or said second catalyst component exhibits C_{2v} symmetry and B₁' and B₂' are the same and are a phenyl group or a substituted phenyl group or said second catalyst component exhibits C_s symmetry and B₁' is a phenyl or substituted phenyl group and B₂' is different from B₁' and is a polyphenyl group or

terphenyl group. A second activating co-catalyst component is provided which may be the same as or different from the first co-catalyst component. The second catalyst component and the second co-catalyst component are contacted with ethylene in a polymerization reaction zone under polymerization conditions to produce a second polymer product which has a different molecular weight characteristic than the corresponding molecular weight characteristic of the first polymer product. This second polymer product is then recovered from the polymerization reaction zone. In one embodiment of the invention, the first catalyst component has C2 symmetry and the second catalyst component has Cs or C2v symmetry to produce a second polymer product which has a higher molecular weight than the first polymer product. In another embodiment, the first catalyst component has C2 or Cs symmetry and the second catalyst component has C2v symmetry to produce a second polymer product having a higher molecular weight than the first polymer product. In yet a further embodiment of the invention, both of the first and second catalyst components have C2 symmetry and the substituent A' of the second catalyst component is bulkier than the substituent A of the first catalyst component to produce a second polymer product of lower molecular weight than that of the first polymer product. In another embodiment of the invention employing catalyst components of C2 symmetry, the groups B₁' and B₂' of the second catalyst component have a lower aromaticity than the groups B₁ and B₂ to produce a second polymer product having a lower molecular weight than the first polymer product.

[0012] In yet another embodiment of the invention, the catalysts each have C2v symmetry. Here, the substituent A' of the second component is bulkier than the substituent A of the first catalyst component with the production of a second polymer product which has a higher molecular weight than that of the first polymer product. In a further embodiment of the

invention, where the first and second catalyst components have Cs symmetry, the group B₁' of the second component has a bulk greater than the group B₁ of the first catalyst component. In addition or alternatively, where the catalyst components have Cs symmetry, the group B₂' of the second catalyst component has a bulk greater than the bulk of the group B₂ of first catalyst component. In both cases, the second polymer product has a higher molecular weight than the molecular weight of the first polymer product. In yet a further embodiment of the invention, there is provided an ethylene polymerization process involving a first transition metal catalyst component characterized by formula (I) above and a second transition metal catalyst component characterized by formula (I) which is different from the first transition metal catalyst component. The first catalyst component is contacted with a first activating co-catalyst component and ethylene in a polymerization reaction zone to produce a first ethylene polymer product. The second catalyst component, which is different from the first transition metal component and an activating co-catalyst component are introduced into a reaction zone which is operated under polymerization conditions to produce a polymer product by polymerization of the ethylene. In one embodiment of the invention, the first and second catalyst components are introduced into the polymerization reaction zone as a mixture. In another embodiment of the invention, the first and second catalyst components are introduced into the polymerization reaction zone sequentially to produce two different polymer products.

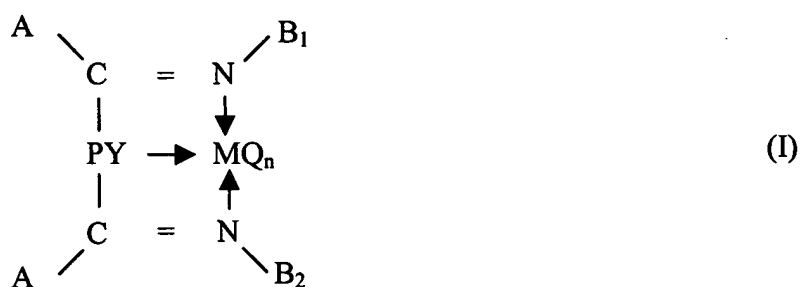
BRIEF DESCRIPTION OF THE DRAWING

[0013] The drawing is a graphical presentation showing molecular weight distributions of polyethylene produced by a C₂ symmetric catalyst, a C_s symmetric catalyst and a C_{2v} symmetric catalyst.

DETAILED DESCRIPTION OF INVENTION

[0014] The present invention involves pyridinyl-bridged bis-imino transition metal catalysts having C₂, C_{2v} and C_s symmetry and their use in the polymerization of ethylene. The ethylene may be polymerized, either through homopolymerization or copolymerization with a C₃₊ alpha olefin, specifically propylene through 1-hexene. The C₂, C_{2v} and C_s symmetric catalyst components of the present invention incorporate transition metals from Groups 4-11 of the Periodic Table of Elements (new notation) and more particularly, transition metals from Groups 8-11 of the Periodic Table of Elements. Preferred transition metals for use in the catalyst components of the present invention are iron, cobalt, nickel and copper with iron and cobalt being particularly preferred.

[0015] The transition metal catalyst components employed in carrying out the present invention incorporate pyridinyl-linked bis-imino ligands which chelate to the transition metal center provided by transition metal M as shown by formula (I):

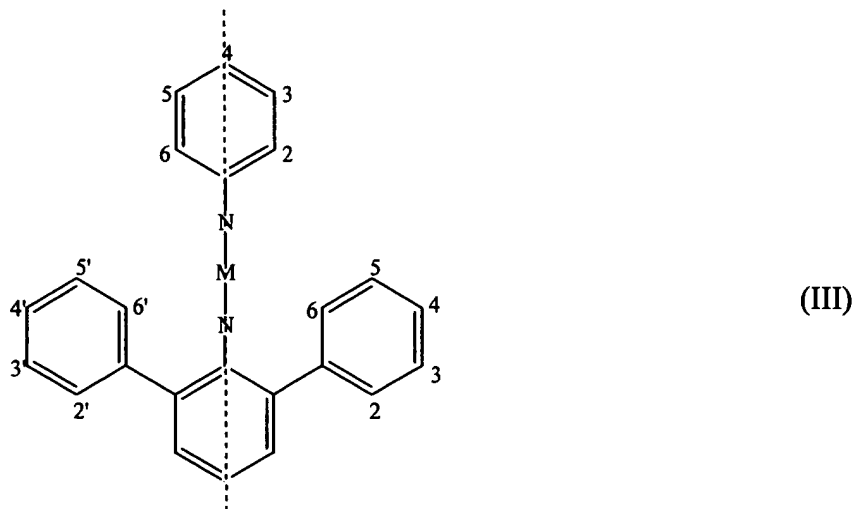


In formula (I), Q is a halogen or a C₁ – C₂ alkyl group. Preferably, Q will take the form of chlorine or bromine with M being iron or cobalt and n being 2. A is a methyl group, a phenyl group, or a substituted phenyl group. For C₂ symmetry, B₁ and B₂ are the same and are a 1-naphthyl group, a substituted 1-naphthyl group, a 5,6,7,8-tetrahydro-1-naphthyl group or an

anthracenyl group as discussed below. The groups B_1 and B_2 may be meso or racemic with respect to the transition metal center.

[0016] For catalysts exhibiting C_{2v} symmetry, B_1 and B_2 are the same and may be a phenyl group or a substituted phenyl group, including a terphenyl group. For the catalyst exhibiting C_{2v} symmetry, the aromatic groups B_1 and B_2 are symmetrical with respect to a plane of symmetry through the coordinating nitrogen atom as described below with respect to C_s symmetry.

[0017] For the transition metal catalyst component exhibiting C_s symmetry, B_1 and B_2 are different. B_1 is a phenyl or substituted phenyl group and B_2 is a polyphenyl group, and preferably a terphenyl group. Thus, in the case of C_s symmetry, the transition metal catalyst component incorporates pyridinyl-linked bis-imino ligand structures which are unbalanced and incorporate a mononuclear aromatic group linked to one nitrogen atom and a polynuclear aromatic group linked to the other nitrogen atom. The mononuclear and polynuclear aromatic groups may be substituted or unsubstituted, but if substituted, each aromatic group is symmetrical with respect to each group's respective coordinating nitrogen atom to provide a ligand structure having C_s symmetry. In C_s symmetry, the plane of symmetry extends through the transition metal and nitrogen atoms of the bis-imino ligand as shown by the following diagram of a bridged phenyl-terphenyl structure as indicated below:









[0018] In diagram (III), the plane of symmetry is indicated by the broken line and is perpendicular to the plane of the paper in which the phenyl and terphenyl groups are schematically shown. With respect to the phenyl group, C_s symmetry is observed if the phenyl group is unsubstituted, mono-substituted at the 4 (directly distal position), di-substituted at the 2,6 positions with the same substituents, or at the 3,5 positions with the same substituents. With respect to the terphenyl group, C_s symmetry is maintained if the terphenyl group is unsubstituted, di-substituted at the distal positions 4 and 4' of the substituent phenyl groups, or substituted on the substituent phenyl groups at the 2 and 2' positions with the same substituent groups, and at the 6 and 6' positions with the same substituent groups, which may be the same or different than the substituents at the 2 and 2' positions. Diagram (III), which schematically shows a phenyl-terphenyl ligand structure in which the substituent phenyl groups are substituted on the primary benzyl group of the terphenyl group at the proximal positions with respect to the nitrogen linkage, is illustrative of embodiments of the invention such as shown by compounds 12-19 below.

[0019] As noted previously, a preferred application of the present invention involves the use of a catalyst of C₂, C_{2v} or C_s symmetry in which the transition metal is iron. This embodiment of the invention is illustrated by the following formula:



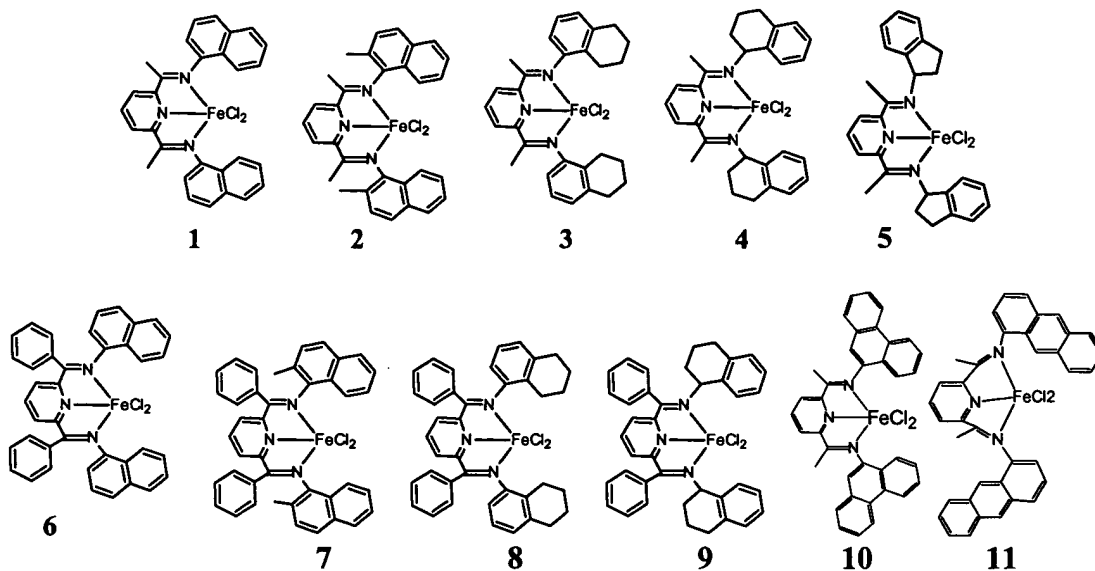
[0020] According to the present invention, a catalyst component of formula (IV) with N,N,N bis-imino-pyridyl ligand, chelating to the iron center with X = Cl or Br, substituents A, B₁, and B₂ are selected to provide a catalyst component that has C₂, C_s or C_{2v} symmetry of the complex. Examples of C₂, C_{2v} and C_s symmetric catalyst components are shown, but not limited to the following compounds 1 through 24.

[0021] In the following exemplary compounds, a methyl group is indicated by , an isopropyl group by  and a tertiary butyl group by . Aromatization of the aromatic group is indicated by  and dearomatization, as in the case of a 5,6,7,8-tetrahydronaphthalene is indicated by , or by .

C₂ Symmetry

[0022] A = methyl, phenyl or substituted phenyl.

[0023] B₁ = B₂ = 1-naphthyl; substituted-1-naphthyl; 5,6,7,8-tetrahydro-1-naphthyl; anthracenyl group.



As indicated by the above examples, the ligand structure may have a meso configuration, as indicated by compounds 1-4 and 6-10 or it may have a racemic configuration, as indicated by compounds 5 and 11.

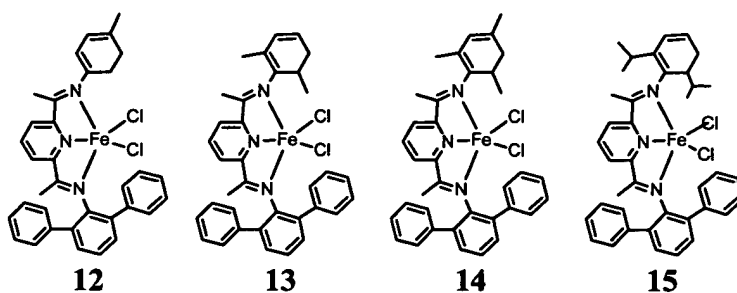
Cs Symmetry

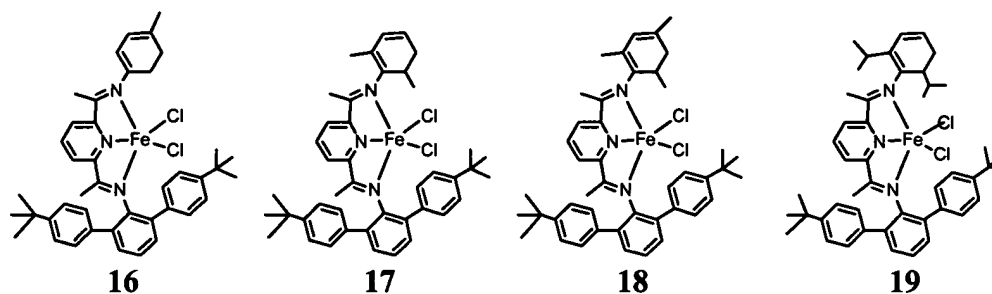
[0024] A = methyl, phenyl or substituted phenyl.

[0025] B₁ is not equivalent to B₂.

[0026] B₁ = phenyl or substituted phenyl group.

[0027] B₂ = polyphenyl group, terphenyl group.

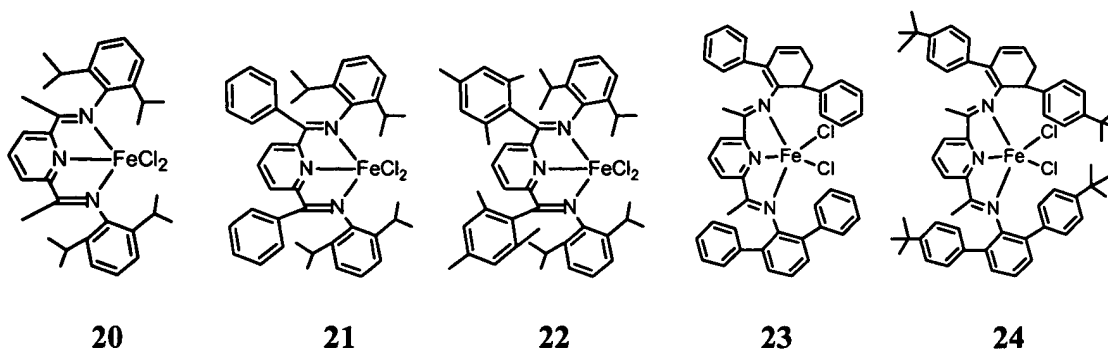




C_{2v} Symmetry

[0028] A = methyl, phenyl or substituted phenyl.

[0029] B₁ = B₂ = phenyl or substituted phenyl group.



[0030] In employing the catalyst components of the present invention in polymerization procedures, they are used in conjunction with an activating co-catalyst. Suitable activating co-catalysts may take the form of co-catalysts such are commonly employed in metallocene-catalyzed polymerization reactions. Thus, the activating co-catalyst may take the form of an alumoxane co-catalyst. Alumoxane co-catalysts are also referred to as aluminoxane or polyhydrocarbyl aluminum oxides. Such compounds include oligomeric or polymeric compounds having repeating units of the formula:



where R is an alkyl group generally having 1 to 5 carbon atoms. Alumoxanes are well known in the art and are generally prepared by reacting an organo-aluminum compound with water, although other synthetic routes are known to those skilled in the art. Alumoxanes may be either linear polymers or they may be cyclic, as disclosed for example in U.S. Patent No. 4,404,344. Thus, alumoxane is an oligomeric or polymeric aluminum oxy compound containing chains of alternating aluminum and oxygen atoms whereby the aluminum carries a substituent, preferably an alkyl group. The structure of linear and cyclic alumoxanes is generally believed to be represented by the general formula $-(\text{Al}(\text{R})-\text{O})-m$ for a cyclic alumoxane, and $\text{R}_2\text{Al}-\text{O}-(\text{Al}(\text{R})-\text{O})m-\text{AlR}_2$ for a linear compound wherein R independently each occurrence is a $\text{C}_1 - \text{C}_{10}$ hydrocarbyl, preferably alkyl or halide and m is an integer ranging from 1 to about 50, preferably at least about 4. Alumoxanes also exist in the configuration of cage or cluster compounds. Alumoxanes are typically the reaction products of water and an aluminum alkyl, which in addition to an alkyl group may contain halide or alkoxide groups. Reacting several different aluminum alkyl compounds, such as, for example, trimethylaluminum and tri-isobutylaluminum, with water yields so-called modified or mixed alumoxanes. Preferred alumoxanes are methylalumoxane and methylalumoxane modified with minor amounts of other higher alkyl groups such as isobutyl. Alumoxanes generally contain minor to substantial amounts of the starting aluminum alkyl compounds. The preferred co-catalyst, prepared either from trimethylaluminum or tri-isobutylaluminum, is sometimes referred to as poly (methylaluminum oxide) and poly (isobutylaluminum oxide), respectively.

[0031] The alkyl alumoxane co-catalyst and transition metal catalyst component are employed in any suitable amounts to provide an olefin polymerization catalyst. Suitable aluminum transition metal mole ratios are within the range of 10:1 to 20,000:1 and preferably within the range of 100:1 to 2,000:1. Normally, the transition metal catalyst component and the alumoxane, or other activating co-catalyst as described below, are mixed prior to introduction in the polymerization reactor in a mode of operation such as described in U.S. Patent No. 4,767,735 to Ewen et al. The polymerization process may be carried out in either a batch-type, continuous or semi-continuous procedure, but preferably polymerization of the ethylene will be carried out in a loop-type reactor of the type disclosed in the aforementioned patent no. 4,767,735. Typical loop-type reactors include single loop reactors or so-called double loop reactors in which the polymerization procedure is carried in two sequentially connected loop reactors. As described in the Ewen et al. patent, when the catalyst components are formulated together, they may be supplied to a linear tubular pre-polymerization reactor where they are contacted for a relatively short time with the pre-polymerization monomer (or monomers) prior to being introduced into the main loop type reactors. Suitable contact times for mixtures of the various catalyst components prior to introduction into the main reactor may be within the range of a few seconds to 2 days. For a further description of suitable continuous polymerization processes which may be employed in carrying out the present invention, reference is made to the aforementioned patent no. 4,767,735, the entire disclosure of which is incorporated herein by reference.

[0032] Other suitable activating co-catalysts which can be used in carrying out the invention include those catalysts which function to form a catalyst cation with an anion comprising one or more boron atoms. By way of example, the activating co-catalyst may take the form of triphenylcarbenium tetrakis(pentafluorophenyl) boronate as disclosed in U.S. Patent

No. 5,155,080 to Elder et al. As described there, the activating co-catalyst produces an anion which functions as a stabilizing anion in a transition metal catalyst system. Suitable noncoordinating anions include $[\text{W}(\text{PhF}_5)]^-$, $[\text{Mo}(\text{PhF}_5)]^-$ (wherein PhF_5 is pentafluorophenyl), $[\text{ClO}_4]^-$, $[\text{S}_2\text{O}_6]^-$, $[\text{PF}_6]^-$, $[\text{SbR}_6]^-$, $[\text{AlR}_4]^-$ (wherein each R is independently Cl, a $\text{C}_1 - \text{C}_5$ alkyl group preferably a methyl group, an aryl group, e.g. a phenyl or substituted phenyl group, or a fluorinated aryl group). Following the procedure described in the Elder et al. patent, triphenylcarbenium tetrakis(pentafluorophenyl) boronate may be reacted with pyridinyl-linked bis-imino ligand of the present invention in a solvent, such as toluene, to produce a coordinating cationic-anionic complex. For a further description of such activating co-catalyst, reference is made to the aforementioned U.S. Patent No. 5,155,080, the entire disclosure of which is incorporated herein by reference.

[0033] In addition to the use of an activating co-catalyst, the polymerization reaction may be carried out in the presence of a scavenging agent or polymerization co-catalyst which is added to the polymerization reactor along with the catalyst component and activating co-catalyst. These scavengers can be generally characterized as organometallic compounds of metals of Groups IA, IIA, and IIIB of the Periodic Table of Elements. As a practical matter, organoaluminum compounds are normally used as co-catalysts in polymerization reactions. Specific examples include triethylaluminum, tri-isobutylaluminum, diethylaluminum chloride, diethylaluminum hydride and the like. Scavenging co-catalysts normally employed in the invention include methylalumoxane (MAO), triethylaluminum (TEAL) and tri-isobutylaluminum (TIBAL).

[0034] As described previously, molecular weight control of the polyethylene product can be achieved through the use of a catalyst having C₂ symmetry, C_s symmetry and C_{2v} symmetry. In general, the use of catalyst exhibiting C₂ symmetry is effective in providing high yields of ethylene polymers having relatively low molecular weights within the range of 500 – 100,000. In using the C₂ symmetric catalyst components, molecular weight control can be effected by changing the bulk of the substituents A, or by changing the aromaticity of the substituents B₁ and B₂ of formula (1). Thus, molecular weight can be decreased when employing C₂ symmetric catalyst components by increasing the bulk of the substituents A or by dearomatization of the substituents B₁ and B₂.

[0035] The C_s symmetric catalyst components provide for high yields of ethylene polymers or copolymers with intermediate molecular weights within the range of 100,000 – 650,000. When using C_s symmetric catalyst components, molecular weight control can be effected by increasing the size and number of electron donative substituents of B₁ and/or B₂.

[0036] The C_{2v} symmetric catalyst components are effective in producing high yields of ethylene polymers or copolymers having relatively high molecular weights within the range of 200,000 – 1,500,000. For the catalyst components of C_{2v} symmetry, molecular weight can be effected by regulating the bulk of the substituents A, with an increase in bulk of these substituents A corresponding to an increase in molecular weight of the resulting polymer product.

[0037] For the C₂, C_s and C_{2v} symmetric catalyst components, molecular weight control can be effected without the need of using substantial amounts of molecular weight regulators such as hydrogen. Small amounts of hydrogen can be, but need not be, used to control

molecular weight. Where hydrogen is used for this purpose, it will be used in amount of less than 5 mole % based upon the ethylene feed and usually within an amount of no more than 2 mole % of the ethylene feed. As indicated by the experimental work described in greater detail below, these very small amounts of hydrogen, which are much less than the amount of hydrogen typically used for molecular weight control, can be used effectively in the present invention.

[0038] The following examples 1-30 are illustrative of polymerization procedures which can be carried out in accordance with the present invention. In Examples 1-7, 15-17 and 21-24, the catalyst component had C₂ symmetry. In Examples 8-10 and 25-28, the catalyst component exhibited C_{2v} symmetry and in Examples 11-14, 18-20 and 29 and 30, the catalyst component exhibited C_s symmetry. As indicated by the following examples, the molecular weight of the polyethylene produced with the catalyst component progressively indicates a general progression in increase when going from C₂ symmetry to C_s symmetry to C_{2v} symmetry. Figure 1 illustrates the effect of the type of symmetry of the catalyst component on the molecular weight of the polyethylene produced. In Figure 1, molecular weight distributions are plotted with the percent of the area, A, on the ordinate and the molecular weight in a logarithmic scale on the abscissa. In Figure 1, curve 2 is a plot of the molecular weight distribution of the polyethylene produced by a C₂ symmetric catalyst component of compound 1, curve 4 is a plot of the molecular weight distribution of polyethylene produced by the C_s symmetric catalyst 13, and curve 6 is a plot of the molecular weight distribution of polyethylene produced by the catalyst component 20, exhibiting C_{2v} symmetry.

[0039] In addition to effecting control of the molecular weight of polyethylene by selection of catalyst symmetry, the molecular weight produced by C₂, C₂ and C_{2v} symmetric catalyst can also be controlled by the addition of hydrogen and 1-hexene. An addition of

hydrogen during the ethylene polymerization increases the activities of the C₂, C_s and C_{2v} catalysts and increases the molecular weight of the polyethylene produced (ex. 15 and 16 for C₂ symmetry; ex. 18 and 19 for C_s symmetry; ex. 21 and 22 for C₂ symmetry; ex. 25 and 26 for C_{2v} symmetry). An addition of 1-hexene to polymerization reactor results in decreasing molecular weight (mostly due to a copolymerization process) (ex. 21 and 23 for C₂ symmetry; ex. 25 and 27 for C_{2v} symmetry). An addition of hydrogen and 1-hexene results in production of polyethylene with low molecular weight in higher yields.

Examples 1-7 – C_s Symmetry

[0040] In examples 1-7, the polymerizations were conducted using an Endeavor reactor. For each catalyst, a stock solution was made by weighing out a specified amount of the iron catalyst in a 20 ml Wheaton bottle and dissolving it in 3 ml of 1,2-dichloroethane followed by diluting it with 17 ml toluene to make a total volume of 20 ml.

[0041] Each polymerization was conducted by injecting a specified amount of the stock catalyst solution that contained 6.08E-05 mmoles of catalyst. The catalyst was then activated with an MAO solution (30 wt.% in toluene) to provide an Al/Fe ratio of 1,000. Isobutane solvent was then added to the reactor and then it was pressured up with ethylene and keeping a total ethylene concentration of 8.0 wt.%. The reactor was heated to 50° C for 30 to 60 minutes. The polymerizations were terminated by venting the reactors. Molecular weight characterizations of polymers produced were obtained by Waters Alliance GPC2000 with refractive index detection. The results of Examples 1-7 are shown in Table 1. In Table 1, the second column provides a descriptive identification of the catalyst, the third column identifies the catalyst by the number structures disclosed previously, the fourth column shows the activity of the catalyst in grams of polyethylene per grams of catalyst component per hour, the fifth and

sixth columns show the number average molecular weight and the weight average molecular weight, respectively, the seventh column presents the “z” average molecular weight (a measure of the high molecular tail of the distribution curve), and the last column shows the molecular weight distribution.

Table 1 Ethylene Homopolymerizations using C2 Symmetric Catalysts in Endeavor

Reactor (50° C, i-butane, Fe/Al = 1/1,000, 30 min)

Examples	Catalyst	Catalyst Number	Activity, g PE/gCat/h	Mn	Mw	Mz	Mw/Mn
1	Bis-naphthyl	1	95,349	3,000	93,951	2,793,905	31.3
2	Bis-2-Me-naphthyl	2	56,899	8,465	91,073	2,117,993	10.8
3	Bis-TH-naphthyl	3	128,524	2,480	8,791	39,846	3.5
4	DibenzPy-bis-naphthyl	6	10,011	3,708	9,969	48,210	6.5
5	DibenzPy-bis-2-Me-naphthyl	7	56,899	3,708	9,969	48,210	2.7
6	DibenzPy-bis-TH-naphthyl	8	54,980	2,286	4,561	13,964	2.0
7	Bis-phen	10	99,583	2,902	11,606	51,000	4.0

Examples 8-10 – C2v Symmetry

[0042] The polymerization procedure used in examples 8-10 is the same as in examples 1-7. The results are shown in Table 2.

Table 2 Ethylene Homopolymerizations using C_{2v} catalysts in Endeavor Reactor (50° C, i-butane, Fe/Al = 1/1,000, 30 min)

Examples	Catalyst	Catalyst Number	Activity, g PE/gCat/h	Mn	Mw	Mz	Mw/Mn
8	i-Pr ₂ ,i-Pr ₂	20	40,452	25,919	639,215	5,506,591	24.7
9	DiBenzPy(i-Pr ₂ ,i-Pr ₂)	21	28,541	68,451	906,132	4,107,013	13.2
10	DiMesPy(i-Pr ₂ ,i-Pr ₂)	22	8,529	33,339	1,070,206	4,474,094	32.1

Examples 11- 14 – C_s Symmetry

[0043] The polymerization procedure for examples 11-14 is the same as in examples 1-7. The results are shown in Table 3.

Table 3 Ethylene Homopolymerizations using C_s Symmetric Catalysts in Endeavor Reactor (50° C, i-butane, Fe/Al = 1/1000, 30 min)

Examples	Catalyst	Catalyst Number	Activity, g PE/gCat/h	Mn	Mw	Mz	Mw/Mn
11	Me ₃ Ph ₂	14	45,037	19,215	626,099	4,889,169	32.6
12	Me ₂ Ph ₂	13	23,869	12,532	200,991	2,893,010	16.0
13	i-Pr ₂ Ph ₂	15	35,351	9,317	309,451	4,257,665	33.2
14	Me ₂ (t-BuPh) ₂	17	42,982				

Examples 15-20 – C₂, C_s Symmetry

[0044] The polymerizations for examples 15-20 were performed in a 4L zipperclave reactor. The reactor was charged with i-butene (1,200 g) and ethylene (100 L). A stock solution of the iron catalyst was prepared by adding MAO (30 wt.% in toluene) to the catalyst sample. The stock solution had an Al/Fe mole ratio of 1,000. Each catalyst was completely soluble and

resulted in a dark reddish-brown solution. For the polymerization run, a desired amount of the catalyst stock solution was charged into a bomb plus an additional amount of toluene to provide an amount of about 5.0 ml. This bomb was identified as bomb #2. Then, 1,000 equivalents of MAO (30 wt.% MAO in toluene) plus an additional amount of toluene to provide a total of about 5.0 ml of solution was charged into another bomb identified as bomb #1. Bomb #1 was first charged as a scavenger into the reactor that contained 7 wt.% of ethylene in isobutane at the specified temperature of 35° C. After approximately 3 minutes, bomb #2 was charged into the reactor at 35° C. The total Al/Fe mole ratio in the polymerization was 2,000. The reaction was left at the set temperature of 35° C until the exotherm began to decrease. As soon as the exotherm started to decrease, the reaction temperature was set to the desired temperature. The results of examples 15-20 are shown in Table 4. In Table 4, the third column shows the amount of catalyst used and the fourth and fifth columns show the temperature in °C and the time and minutes of the polymerization run. The amount of hydrogen, where used, as a mole fraction of the ethylene is shown in the sixth column, and the yields in grams are shown in the seventh column, along with the activity of the catalyst in grams of polyethylene per grams of catalyst per hour in the eighth column. The last four columns present data for Mn, Mw, Mz and Mw/Mn, as described previously.

Table 4 Ethylene Homopolymerizations in 4L Bench Reactor (50° C, i-butane, Fe/Al = 1/1000, 30 min, 2mg of catalyst). Hydrogen and Temperature Effect on MW

Ex.	Catalyst	Amount, mg	T, ° C	Time, min	H ₂ /C ₂	Yield, g	Activity, g PE/gCat/h	Mn	Mw	Mz	Mw/Mn
15	1 Bis-naphthyl	2.0	50	60	0	272	73,440	2,800	19,314	164,368	6.9
16	1	2.0	50	60	0.006	228	61,500	4,114	68,464	1,014,445	16.7
17	1	2.0	80	60	0	106	28,620	2,750	11,268	61,696	4.1
18	13 Me ₂ Ph ₂	2.0	50	60	0	29	8,990	26,505	253,921	1,987,142	9.6
19	13	2.0	50		0.006	35	10,850	24,648	282,117	2,738,669	11.4
20	13	2.0	80	60	0	16	4,960	18,056	138,612	895,348	7.7

Examples 21-30 – C₂, C_{2v}, C_s Symmetry

[0045] The polymerization procedure used in examples 21-30 is the same as in examples 15-20. The results produced in examples 15-20 are summarized in Table 5. Table 5 corresponds to the data presented in Table 4, with the exception that a column showing the ml of 1-hexene (where used) is included as column six.

Table 5 Ethylene Homopolymerization and Copolymerization with Hexene-1 in 4L Bench**Reactor (80° C, i-butane, Fe/Al = 1/1000)**

Ex.	Catalyst	Amount, mg	Time, min	H ₂ /C ₂	Hexene-1, ml	Yield, g	Activity, g PE/gCat/h	Mn	Mw	Mz	Mw/Mn
21	2 Bis-2-Me-naphthyl	0.15	30	0	0	283	3,773,333	5,500	66,917	1,597,325	12.2
22	2	0.15	30	0.005	0	550	7,333,333	5,704	77,457	2,175,146	13.6
23	2	0.15	30	0	40	517	6,893,333	5,363	30,397	578,794	5.7
24	2	0.15	30	0.006	40	546	7,280,000	5,369	34,980	807,798	6.5
25	21 iBenzPy(iPr ₂)(iPr ₂)	1.0	40	0	0	3	4,500	13,394	121,401	1,524,929	9.1
26	21	1.0	48	0.005	0	9	11,250	17,519	186,717	2,362,456	10.7
27	21	5.0	30		40	14	5,600	8,671	97,177	1,494,585	11.2
28	21	3.0	30	0.006	40	23	15,541	9,788	93,139	1,322,515	9.52
29	14 (Me ₃)(Ph ₂)	0.5	30	0	0	39	156,000	14,928	243,771	2,271,752	16.3
30	17 (Me ₂)(tBuPh ₂)	0.5	30	0	0	259	1,195,385	18,640	273,711	2,468,959	14.7

[0046] The following examples indicate the preparation of pyridinyl bis-imino ligand structures and their corresponding iron dichloride complexes. Examples 31-44 exhibit the preparation of complexes having C₂ symmetry, examples 45-52 exhibit the preparation of complexes having C_s symmetry, and examples 53-56 exhibit the preparation of catalyst components having C_{2v} symmetry.

Example 31 – Preparation of 2,6-bis[1-(2-Me-1-naphthylimino)ethyl]pyridine

[0047] 2,6-Diacetylpyridine (0.33 g, 2.0 mmol) and 2-methyl-1-iminonaphthylamine (1.99 g, 10.7 mmol) were added to a round-bottom flask with 20 ml of ethanol. 5 Drops of glacial acetic acid were added, the flask was sealed and the solution was stirred for 4 days. The solvent was removed under vacuum. The ligand was isolated after column chromatography (hexane/ethyl acetate = 5/1) to provide a yield of 0.42 g.

Example 32 – Preparation of 2,6-bis[1-(2-Me-1-naphthylimino)ethyl]pyridine iron dichloride
(complex 2)

[0048] The ligand from example 31 (0.42 g, 0.95 mmol) was dissolved in THF (20 ml). FeCl₂ (120.9 mg, 0.95 mmol) was added to the ligand solution. The reaction mixture was stirred for 2 hours at room temperature. A dark blue-green suspension was formed. The solvent was removed under vacuum and the solid residue was crystallized from CH₂Cl₂/hexane to give the desired complex 2.

Example 33 – Preparation of 2,6-bis[1-(5,6,7,8-tetrahydro-1-naphthylimino)ethyl]pyridine

[0049] 2,6-Diacetylpyridine (0.54 g, 3.31 mmol) and 5,6,7,8-tetrahydro-1-naphthylimine (1.46 g, 10 mmol) were added to a round-bottom flask with 20 ml of ethanol. 5 Drops of glacial acetic acid were added, the flask was sealed and the solution was stirred for 3 days. The solvent was removed under vacuum. The ligand was isolated after column chromatography (hexane/ethyl acetate = 5/1) to provide a yield of 1.42 g.

Example 34 – Preparation of 2,6-bis[1-(5,6,7,8-tetrahydro-1-naphthylimino)ethyl]pyridine iron
dichloride (complex 3)

[0050] The ligand from example 33 (0.65 g, 1.54 mmol) was dissolved in CH₂Cl₂ (20 ml). FeCl₂ · 4H₂O (0.35 g, 1.76 mmol) 20 ml of methanol was added to the ligand solution. The reaction mixture was stirred for 2 hours at room temperature. A dark blue-green suspension was formed. The solvent was removed under vacuum and the solid residue was crystallized from CH₂Cl₂/hexane to give the desired complex 3.

Example 35 – Preparation of 2,6-dibenzoylpyridine

[0051] 2,6-pyridinedicarbonyl dichloride (6.12 g, 30.0 mmol) in benzene (60 ml) was added to AlCl_3 (12.2 g, 91.5 mmol) in benzene (50 ml). The reaction mixture was refluxed for 6 hours. The reaction was quenched with an aqueous NaHCO_3 solution. The organic layer was extracted with ether (3x70 ml) and dried over Na_2SO_4 and the solvent was distilled under low vacuum. 2,6-benzoylpyridine was isolated as a solid (90%).

Example 36 – Preparation of 2,6-di(2,4,6-mesityloyl)pyridine

[0052] 2,6-pyridinedicarbonyl dichloride (6.12 g, 30.0 mmol) in mesitylene (60 ml) was added to AlCl_3 (12.2 g, 91.5 mmol). The reaction mixture was refluxed for 6 hours. The reaction was quenched with an aqueous NaHCO_3 solution. The organic layer was extracted with ether (3x70 ml) and dried over Na_2SO_4 and the solvent was distilled under low vacuum. The column chromatography (hexane/ethyl acetate = 5:1) gave a solid product. ^1H NMR and GC analysis indicated the presence of several products. ^1H NMR (CDCl_3) (signals belong to desired pyridine): δ 8.3-6.5 (H_{arom} , $\text{H}_{\text{pyridine}}$), 2.31 (s, 6H, Me), 1.98 (s, 6H, Me), 1.81 (s, 6H, Me).

Example 37 – Dibenzoylbis(1-naphthylimino)pyridine

[0053] TiCl_4 (0.4 ml, 3.5 mmol) in toluene (20 ml) was added to a mixture of dibenzoylpyridine (0.91 g, 3.2 mmol) and 1-naphthylamine (2.90 g, 17 mmol) in toluene (50 ml) at 0°C . After the addition was complete, the reaction was stirred at room temperature for 1 hour and then under refluxed for 3 hours. The solid was filtered and washed with toluene. The solvent was removed under vacuum. The ligand was isolated after the column chromatography (hexane/ethyl acetate = 5/1) to produce a yield of 0.65 g.

Example 38 – 2,6-Dibenzoylpyridine-bis(1'-naphthylimino)iron (II) Chloride (complex 6)

[0054] The ligand from example 37 (0.65 g, 1.08 mmol) was dissolved in THF (20 ml). FeCl₂ (140 mg, 1.10 mmol) was added to the ligand solution. The reaction mixture was stirred for 3 hours at room temperature. A dark blue-green suspension was formed. The solvent was removed under vacuum, and the solid residue was crystallized from CH₂Cl₂/hexane to give complex 6.

Example 39 – Dibenzoylbis(2'-methyl-1'-naphthylimino)pyridine

[0055] TiCl₄ (0.4 ml, 3.5 mmol) in toluene (20 ml) was added to a mixture of dibenzoylpyridine (0.91 g, 3.2 mmol) and 2-methyl-1-naphthylamine (2.26 g, 19 mmol) in toluene (50 ml) at 0° C. After the addition was complete, the reaction was stirred at room temperature for 1 hour and then under reflux for 5 hours. The solid was filtered and washed with toluene. The solvent was removed under vacuum. The ligand was isolated after column chromatography (hexane/ethyl acetate = 5/1) to provide a yield of 0.60 g.

Example 40 – 2,6-Dibenzoylpyridine-bis(2'-methyl-1'-naphthylimino)iron (II) Chloride (complex 7)

[0056] The ligand from example 39 (0.27 g, 0.43 mmol) was dissolved in THF (20 ml). FeCl₂ (60 mg, 0.47 mmol) and added to the ligand solution. The reaction mixture was stirred overnight at room temperature. A dark blue-green suspension was formed. The solvent was removed under vacuum and the solid residue was crystallized from CH₂Cl₂/hexane to give complex 7.

Example 41 – Dibenzoylbis(5',6',7',8'-tetrahydro-1'-naphthylimino)pyridine

[0057] TiCl_4 (0.4 ml, 3.5 mmol) in toluene (20 ml) was added to a mixture of dibenzoylpyridine (0.84 g, 2.9 mmol) and 4,5,6,7-tetrahydro-1-naphthylamine (2.64 g, 18 mmol) in toluene (70 ml) at 0° C. After the addition was complete, the reaction was stirred at room temperature for 1 hour and then under reflux for 4 hours. The solid was filtered and washed with toluene. The solvent was removed under vacuum. The ligand was isolated after column chromatography (hexane/ethyl acetate = 5/1) to provide a yield of 0.69 g.

Example 42 – 2,6-Dibenzoylpyridine-bis(5',6',7',8')-tetrahydro-1'-naphthylimino)iron (II)

Chloride (complex 9)

[0058] The ligand from example 41 (0.65 g, 1.06 mmol) was dissolved in THF (20 ml). FeCl_2 (150 mg, 1.18 mmol) was added to the ligand solution. The reaction mixture was stirred overnight at room temperature. A dark blue-green suspension was formed. The solvent was removed under vacuum and the solid residue was crystallized from CH_2Cl_2 /hexane to give complex 9.

Example 43 – 2,6-bis[1-(9-phenanthrene-imino)ethyl]pyridine

[0059] 2,6-Diacetylpyridine (0.25 g, 1.53 mmol) and 9-aminophenanthrene (0.59 g, 3.06 mmol) were added to a round-bottom flask with 20 ml of ethanol. 5 Drops of glacial acetic acid were added, the flask was sealed and the solution was refluxed for 72 hours. The solvent was removed under vacuum. Toluene (15 ml) and molecular sieves were added. The reaction mixture was heated under reflux for 3 days. The solvent was removed under the vacuum, and the solid residue was crystallized from CH_2Cl_2 /hexane to give the desired ligand.

Example 44 – Preparation of iron bis-imine (9-phenanthrene) (complex 10)

[0060] Bis-imine (9-phenanthrene) ligand from example 43 (0.30 g, 0.58 mmol) and iron dichloride (II) (75 mg) in THF (10 ml) were stirred for 4 hours at 30° C. The solvent was removed under vacuum. The solid residue was crystallized from CH₂Cl₂/hexane to give complex 10.

Example 45 – Preparation of 2-[1-(2,6-dimethylphenylimino(ethyl)-6-[1-(2,6-diphenylphenylimino)ethyl]pyridine

[0061] 2-Acetyl-6-[1-(2,6-diphenylphenylimino)ethyl]pyridine (1.70 g, 4.36 mmol), 2,6-methylaniline (2.3 g) and a catalytic amount of p-toluenesulfonic acid monohydrate in benzene (30 ml) were heated under reflux for two days. The solvent was removed under vacuum. Double crystallization CH₂Cl₂/pentane (1:3) gave the desired ligand (0.33 g). ¹H NMR (CDCl₃): δ 8.34 (d, 1H, H_{pyr}), 8.08 (d, 1H, H_{pyr}), 7.77 (t, 1H, H_{pyr}), 7.5-6.9 (16H, H_{arom}), 2.06 (s, 3H, CH₃-C=N), 2.00 (s, 6H, CH₃), 1.89 (s, 3H, CH₃-C=N).

Example 46 – Preparation of 2-[1-(2,6-dimethylphenylimino(ethyl)-6-[1-(2,6-diphenylphenylimino)ethyl]pyridine iron dichloride (complex 13).

[0062] The same procedure as in example 40 was repeated except the reaction was conducted by using the ligand from example 45.

Example 47 – Preparation of 2-[1-(2,4,6-trimethylphenylimino(ethyl)-6-[1-(2,6-diphenylphenylimino)ethyl]pyridine

[0063] The same procedure as in example 45 was repeated except that the reaction was conducted by using trimethylaniline. ¹H NMR (CD₂Cl₂): δ 8.33 (d, 1H, H_{pyr}), 8.10 (d, 1H,

H_{pyr}), 7.81 (t, 1H, H_{pyr}), 7.6-6.9 (15H, H_{arom}), 2.19 (s, 3H, CH₃ from Ph), 2.14 (s, 6H, CH₃ from Ph), 2.06 (s, 3H, CH₃-C=N), 1.92 (s, 3H, CH₃-C=N).

Example 48 – Preparation of 2-[1-(2,4,6-trimethylphenylimino)ethyl]-6-[1-(2,6-diphenylphenylimino)ethyl]pyridine iron dichloride (complex 14)

[0064] The same procedure as in example 40 was repeated except the reaction was conducted by using the ligand from example 47.

Example 49 – Preparation of ligand: 2-[1-(2,6-diisopropylphenylimino(ethyl)-6-[1-(2,6-diphenylphenylimino)ethyl]pyridine

[0065] The same procedure as in example 45 was repeated except that reaction was conducted by using 2,6-diisopropylaniline. ¹H NMR (CDCl₃): δ 8.31 (d, 1H, H_{pyr}), 8.07 (d, 1H, H_{pyr}), 7.77 (t, 1H, H_{pyr}), 7.5-7.0 (16H, H_{arom}), 2.70 (sept, 2H, CH(CH₃)₂), 2.07 (s, 3H, CH₃-C=N), 1.89 (s, 3H, CH₃-C=N), 1.13 (t, 12H, CH(CH₃)₂).

Example 50 – Preparation of 2-[1-(2,6-diisopropylphenylimino(ethyl)-6-[1-(2,6-diphenylphenylimino)ethyl]pyridine iron dichloride (complex 15)

[0066] The same procedure as in example 40 was repeated except the reaction was conducted by using the ligand from example 49.

Example 51 – Preparation of 2-[1-(2,6-dimethylphenylimino(ethyl)-6-[1-(2,6-bis(4-t-butylphenyl)imino)ethyl]pyridine

[0067] The same procedure as in example 45 was repeated except that reaction was conducted by using 2-acetyl-6-[1-(2,6-bis(4-t-butylphenyl)imino)ethyl]pyridine and 2,6-dimethylaniline.

Example 52 – Preparation of 2-[1-(2,6-dimethylphenylimino(ethyl))-6-[1-(2,6-bis(4-t-butylphenyl)imino)ethyl]pyridine iron dichloride (complex 17)]

[0068] The same procedure as in example 40 was repeated except the reaction was conducted by using the ligand from example 51.

Example 53 – Preparation of 2,6-Dibenzoylbis(2',6'-diisopropylphenylimino)pyridine

[0069] TiCl_4 (0.4 ml, 3.5 mmol) in toluene (20 ml) was added to a mixture of dibenzoylpyridine (0.91 g, 3.2 mmol) (from example 35) and 2,6-diisopropylaniline (3.6 ml, 19 mmol) in toluene (50 ml) at 0° C. After the addition was complete, the reaction was stirred at room temperature for 1 hour and then under reflux for 10 hours. The solid was filtered and washed with toluene. The solvent was removed under vacuum. The residue was crystallized from methanol at -10° C to give the ligand (0.80 g).

Example 54 – Preparation of 2,6-dibenzoylpyridine-bis(2',6'-diisopropylphenylimino)iron (II) chloride (complex 21)

[0070] The ligand from example 53 (0.50 g, 0.83 mmol) was dissolved in EtOH (20 ml). $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.20 g, 1.0 mmol) was dissolved in EtOH (10 ml) and added to the ligand solution. The reaction mixture was stirred for 1 hour at room temperature. The solvent was removed under vacuum and THF (30 ml) was added. The reaction mixture was stirred overnight. A dark blue suspension was formed. The solvent was removed under vacuum and the solid residue was crystallized from CH_2Cl_2 /hexane to give complex 21.

Example 55 – Preparation of 2,6-mesitylbis(2',6'-diisopropylphenylimino)pyridine

[0071] The same procedure as in example 53 was repeated except the reaction was conducted by using the compound from example 36.

Example 56 – Preparation of 2,6-mesitylbis(2',6'-diisopropylphenylimino)pyridine iron
dichloride (complex 22)

[0072] The same procedure as in example 54 was repeated except the reaction was conducted by using the compound from example 55.

[0073] As indicated by the previously described experimental work, changes in symmetry of the catalyst component employed in the polymerization procedure can be used to effect changes in molecular weight of the polymer product. Thus, a first catalyst component of C₂ symmetry can be used to produce a first polymer product, a second catalyst component can be employed to produce a second polymer product of higher molecular weight, and yet a third catalyst component of C_{2v} symmetry can be employed to produce a third polymer product of yet higher molecular weight.

[0074] Further, within each symmetry class, the ligand structure can be varied to effect changes in molecular weight. Thus, the invention can be carried out employing first and second catalyst components having C₂ symmetry as indicated by formulas (I) and (II) above. Here, the substituent A₁ of the second catalyst component can be bulkier than the substituent A of the first catalyst component to produce a second polymer product which has a lower molecular weight than the molecular weight of the first polymer product. In addition, control of molecular weight can be effected by changes in the aromaticity of the groups B and B₂. Thus, the second catalyst may exhibit groups B₁' and B₂' which has a lower aromaticity than the groups B₁ and B₂ of the first catalyst to produce a second polymer having a lower molecular weight than the molecular weight of the first polymer product.

[0075] For catalysts with Cs symmetry, first and second catalyst components can be employed in which the group B₁' of the second catalyst component has a bulk which is greater than the group B₁ of the first catalyst component to produce a second polymer product which has a higher molecular weight than the molecular weight of the first polymer product. Similar changes can be made in the groups B₂ and B₂' of the first and second catalyst component. Thus, group B₂' of the second component can be formulated to have a bulk which is greater than the group B₂ of the first catalyst component to produce a second polymer product which has a higher molecular weight than the molecular weight of the first polymer product. Alternatively, or in addition, with a catalyst that has Cs symmetry, the group B₁' of the second catalyst component can have a bulk that is greater than B₁ of the first catalyst component to produce a second polymer product which has a higher molecular weight than the molecular weight of the first polymer product.

[0076] Where the catalyst component has a C_{2v} symmetry, the first and second catalyst components corresponding to formulas (I) and (II) can be employed in which the substituent A' of the second catalyst component is bulkier than the substituent A of the first catalyst component to produce a second polymer product which has a higher molecular weight than the molecular weight of the first polymer product.

[0077] The designations "first" and "second" with respect to polymerization procedures, catalyst or co-catalyst components, or polymer products are distinguishing adjectives and are not intended to designate the order or sequence in which the polymerization reactions are carried out. Thus, where a common reactor is employed, the second catalyst component may be

introduced into the reactor to produce a second polymer product before or after the production of the first polymer product. Also, the polymerization procedures involving the first and second catalyst components, co-catalyst components and polymer products can be carried out in separate reactors, either concurrently or consecutively in the different reactors. Thus the “first” polymerization procedure may be carried out in a loop-type reactor, while the “second” polymerization can be carried out in a second loop-type reactor in conjunction with the same or different downstream processing procedures involving the treatment of polymer fluff in the extrusion and pelletization of the polymer product.

[0078] The polymer products, including ethylene homopolymers and ethylene- C_{3+} alpha olefin copolymers, such as ethylene propylene copolymers, produced by the polymerization process of the present invention, can be used to produce a wide variety of end use products. Thus, the polymer products may be employed to produce blow-molded products or injection-molded products, such as bottles for milk, food, and detergents and the like, housewares, such as toys and pails and various extruded products. Such extruded products include film products for producing grocery and merchandise bags, packaging for food products, sheets for truck bed liners and luggage, shipping containers and bulk storage tanks. Large blow molded parts which can be produced include articles such as shipping containers and bulk storage tanks, and pipes, including high pressure pipes for use in various industrial applications such as for sewer pipes and pipes for gas, oil, and water transport applications. The polyethylene products are characterized by a high electrical resistivity and thus may be used in insulating applications such as insulating coatings on electrical wiring products. Molded ethylene homopolymer or copolymer products produced in accordance with the present invention can also be used to provide various automotive components by injection moldings, including, without

limitation, automobile or truck dashboards and interior trim moldings. Where the polymer products produced in accordance with the present invention are used to make end use products by injection molding, various injection molded components may be made by injecting the polymer product into molds conforming to the shape of the article to be manufactured. As indicated, various articles may also be produced by blow molding to produce containers, bottles and the like, or by extrusion to form thin film products. In addition to films and the like, the ethylene homopolymer or copolymer product produced by the process of the present invention may be used to produce various fibers, meshes and textile materials as well as articles of apparel, such as gowns, masks, gloves and the like.

[0079] Having described specific embodiments of the present invention, it will be understood that modifications thereof may be suggested to those skilled in the art, and it is intended to cover all such modifications as fall within the scope of the appended claims.